Nanoscale Res Lett (2010) 5:332–337
DOI 10.1007/s11671-009-9484-6

NANO EXPRESS

Avoiding Loss of Catalytic Activity of Pd Nanoparticles Partially Embedded in Nanoditches in SiC Nanowires

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Received: 28 September 2009 / Accepted: 28 October 2009 / Published online: 15 November 2009

Abstract Nanoditches from selective etching of periodically twinned SiC nanowires were employed to hinder the migration and coalescence of Pd nanoparticles supported on the nanowires, and thus to improve their catalytic stability for total combustion of methane. The results show that the etched Pd/SiC catalyst can keep the methane conversion of almost 100% while the unetched one has an obvious decline in the catalytic activity from 100 to 82% after ten repeated reaction cycles. The excellent catalytic stability originates from the limitation of the nanoditches to the migration and growth of Pd nanoparticles.

Keywords SiC nanowires · Selective etching · Pd nanoparticles · High catalytic stability

Introduction

Noble metal nanoparticles dispersed on inert supports usually exhibit high chemical activity in heterogeneous catalyst as well as fuel cell applications. However, the metal nanoparticles migrate and aggregate easily on the supports, thus their chemical activity decreases rapidly. For example, the growth of Pt nanoparticles in the cathode catalyst of fuel cell is one of the major factors resulting in the degradation of catalytic performance [1, 2]. Au nanoparticles with a size below 5 nm exhibit very high catalytic activity, and their catalytic activity shows a sharp reduction when the particle size becomes larger than 5 nm [3, 4]. Similarly, the increase in activity of Pd-based catalysts is found to depend on the decrease of the size of PdO crystallites [5, 6]. In addition, the deactivation of catalysts can be aggravated by the coke deposition, which is formed more easily over larger metal particles [7]. Therefore, the control of migration and aggregation of metal nanoparticles on the supports remains a challenging problem in heterogeneous catalysis. Recently, different routes have been proposed to improve their stability. The Somorjai group designed a high-temperature-stable model catalytic system consisting of a Pt core coated with a mesoporous silica shell and found that the core–shell particles exhibited high catalytic activity and stability [8]. The same group also proposed to stabilize Rh nanoparticle catalyst using poly(vinylpyrrolidone) for CO oxidation [9]. The Xia group designed Pt–Pd bimetallic nanodendrites to stabilize Pt nanoparticles [10]. In industrial catalysts, a practicable solution to the problem is to enhance the interaction between metals and supports by modification of the support surface; however, the metal nanoparticles may react with the supports or modifiers to form low-activity phases, and resulting in a decrease of their catalytic activity [11, 12].

Catalytic combustion of methane is the process in which methane is oxidized to CO_2 and H_2O at a low temperature. It is a promising solution to the removal of low-concentration methane from gas mixtures due to lower emissions

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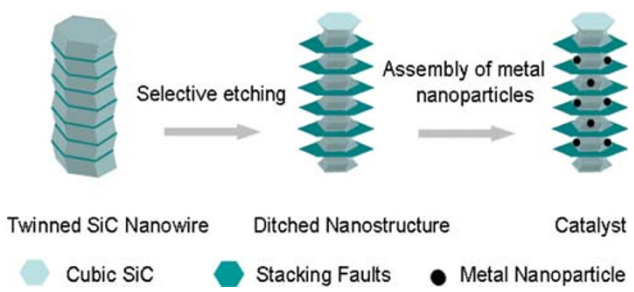
of NO_x, CO, and unburned hydrocarbons [13, 14]. Supported Pd catalysts have been found to have excellent catalytic activity for the process, and the supports generally are oxides, such as SiO_2, Al_2O_3, silica-alumina, and different zeolithic frameworks [13, 14]. However, the catalytic combustion of methane is a strongly exothermic reaction, which requires that the supports can disperse the reaction heat efficiently. Unfortunately, the supports mentioned earlier are thermal insulators and the reaction heat accumulated on isolated metal nanoparticles makes them sintered together easily. Therefore, the reactions between the Pd nanoparticles and the supports remain a problem [11, 12]. To solve this problem, thermal conductive SiC and Si_3N_4 have been employed as the catalyst supports [15, 16]. Yet, Pd nanoparticles migrate and coalesce easily on SiC or Si_3N_4 surfaces, resulting in a decrease in catalytic activity again.

Cubic SiC nanowires usually contain a high density of periodical stacking faults perpendicular to the growth direction [17–20]. These stacking faults enable the nanowires to have different acid resistance from the regions between the faults. By selective etching, different research groups have prepared a variety of patterned SiC nanostructures [21–23]. In our previous work, it was found that the periodically twinned SiC nanowires could be converted into periodically nanoditched nanowires by HNO_3 + HF etching [19]. Therefore, we think that the nanoditched nanowires can be used to design a novel nanostructured catalyst by assembling metal nanoparticles into the nanoditched SiC nanowires, as shown in Scheme 1. The nanoditched nanostructure is expected to hinder the migration and coalescence of metal nanoparticles on the nanowire supports, in turn to achieve a stable catalytic activity.

In this work, we employed nanoditched SiC nanowires to design the catalyst for catalytic combustion of methane and demonstrated that the novel nanostructures can effectively hinder the migration and growth of Pd nanoparticles and has greatly improved their catalytic stability.



Scheme 1 Schematic diagram of the novel nanostructured catalyst: Pd nanoparticles are anchored in the ditches of the nanowires

Experimental Section

Periodically twinned SiC nanowires were prepared by the carbothermal reduction of a carbonaceous silica xerogel precursor from tetraethoxysilane and biphenyl [19]. The nanowires were etched in the mixture of HF (38–40%) and HNO_3 (65%) solutions with a volume ratio of 3:1 at 60°C for 10 min and 85°C for 30 min, respectively. After etching, the nanowires were washed with deionized water and dried at 110°C. The impregnation method was used to prepare Pd/SiC catalyst. Firstly, 0.4 g of the etched or unetched SiC was added into 20 ml of $Pd(NO_3)_2{\cdot}2H_2O$ aqueous solution (0.05 wt.%) under stirring for 12 h. Afterward, the mixture was dried at 110°C for 12 h and then calcined in air at 500°C for 4 h. By this method, the catalyst has a Pd loading of 1 wt.%.

The catalytic performance of the Pd/SiC catalysts were tested in a fixed-bed quartz reactor with an inner diameter of 8 mm at atmospheric pressure, and the mixture of O_2 (20%)/CH_4 (1%)/N_2 (79%) was used as the feedstock. A weight of 300 mg of the catalyst was packed between two layers of quartz wool. The hourly space velocity was controlled to be 12,000 h^{-1}. Since the deactivation of a supported SiC catalyst usually demands a long time, a cyclic reaction method was used to estimate the catalyst stability. In this method, the catalyst was programmed heated to a temperature at which the reaction obtained a near 100% methane conversion. In the heating process, the methane conversion was measured at different temperature. Afterward, the reactor was cooled down to the temperature at which the catalyst just became inactive, and then the next reaction cycle began again.

The fresh and used catalysts were studied by transmission electron microscopy (TEM, JEM-2010). The sample was firstly ultrasonically dispersed in ethanol for 20 min. Afterward, a droplet of the suspension was dropped to a lacey carbon-coated copper grid and dried for TEM observation.

Results and Discussion

The SiC nanowires, having a hexagonal cross section, are characterized by a zigzag arrangement of periodically twinned segments with a rather uniform thickness along the entire growth length. According to our previous work [19], the zigzag nanowires are formed by periodical twins, and the rotation angle of two neighboring cubic segments is 141°, which is twice the interplanar angle of 70.5° between {111} planes. The HF and HNO_3 mixture etches the cubic segments between the twin boundaries. The unetched twin boundaries thus become separated platelets or fins standing on the etched nanowires. Therefore, the etched nanowires

show a morphology of repeating fins as reported in literature [19, 22]. However, the etched sample under the etching condition of 60°C for 10 min did not show a fin-like structure, instead many shallow nanoditches were formed, and these nanoditches were distributed periodically on the entire nanowires (see Fig. 1). This is because the present etching is carried out at a lower temperature and in a shorter time.

Figure 1 shows TEM images of the as-prepared Pd/SiC catalyst (etched at 60°C for 10 min). In Fig. 1a, it can be seen that homogeneous Pd nanoparticles are dispersed on the nanowire surface. Moreover, almost all the Pd nanoparticles are partially embedded in the nanoditches, and the nanoditches have a negative curvature of about 10 nm (Fig. 1b). The Pd nanoparticles have a diameter ranging from 2.4 to 3.6 nm and an average size of 2.9 nm according to our statistical analysis. High-resolution TEM image (Fig. 1c) reveals the highly crystalline features of the support as well as the Pd particles. The spacing between two adjacent lattice fringes in the support is 0.254 nm, which corresponds well to the interplanar spacing of the (111) plane of β-SiC. The partially embedded nanoparticle gives the fringes of a lattice spacing of 0.224 nm, which is indexed as that of the (111) planes of face-centered cubic Pd.

The catalytic performance of the Pd/SiC catalyst was studied by the catalytic combustion of methane. For the nanoditched Pd/SiC catalyst (etched at 60°C for 10 min), the reaction cycle started from 270°C and ended at 390°C. This is to say that the catalyst has obtained a methane conversion of almost 100% at 390°C in the first reaction cycle. This result is slightly better than that previously reported by Méthivier et al. (~425°C) [15]. Figure 2a shows the tested results of the catalyst stability. From the

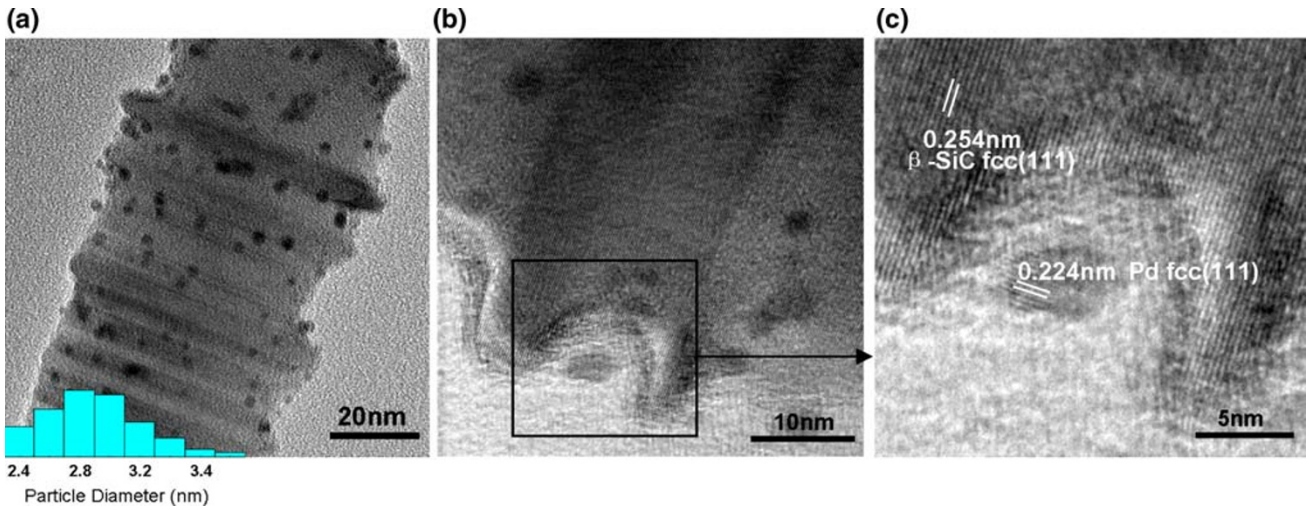


Fig. 1 Different magnification TEM *images* of the as-prepared Pd/SiC catalyst showing that the homogeneous Pd nanoparticles embedded in the ditches on the etched nanowires

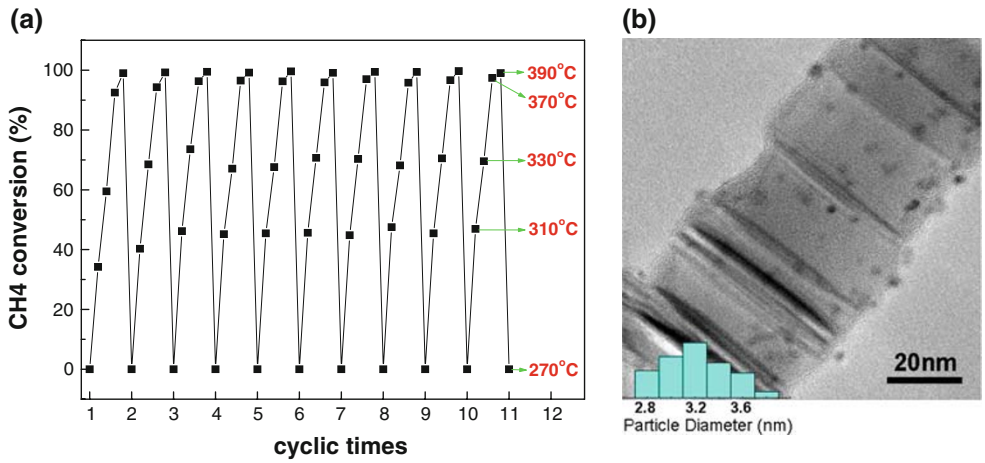


Fig. 2 Cyclic reaction results (**a**) of the Pd/SiC catalyst (etching at 60°C for 10 min) showing the catalyst exhibits excellent activity and stability; TEM images (**b**) of the used catalyst showing the particle size only have a little change after reaction

figure, the catalyst still keeps a methane conversion of almost 100% after 10 reaction cycles, indicating that the catalyst has excellent stability in the catalytic combustion of methane. The TEM image of the catalyst used after 10 cycles is shown in Fig. 2b. From the image, the Pd nanoparticles are still dispersed uniformly on the support. By the statistical analysis, the particles have an average size of 3.2 nm, which is slightly larger than that of the fresh catalyst of 2.9 nm (Fig. 1a).

For comparison, we also used unetched SiC nanowires as the support of Pd/SiC catalyst. Figure 3a shows a TEM image of the as-prepared catalyst. By the statistical analysis, the Pd nanoparticles on the unetched SiC nanowires have a diameter ranging from 4.1 to 9.7 nm and an average size of 6.7 nm, which is lager than that on the etched SiC nanowires. Generally speaking, the surface of the unetched nanowires is smoother than that of the etched; therefore, the initially formed Pd particles on the unetched nanowires have a smaller contact area and thus less adhesion with the support. During the catalyst calcination (500°C, 4 h), these initial particles have undergone a migration and coalescence process. As a result, the Pd particles on the unetched support are larger than those on the etched support.

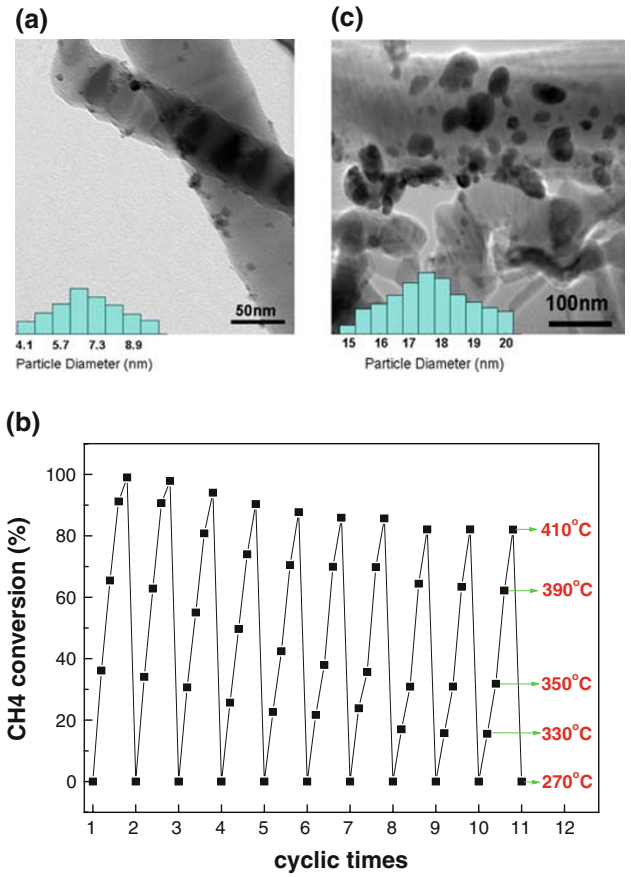


Fig. 3 TEM images of fresh (**a**) and used (**c**) Pd/SiC catalyst (unetched) showing that Pd nanoparticles seriously migrated and grew on the smooth surface of the nanowire support after reaction; (**b**) the test results showing the activity and stability of the catalyst sharply decreased in the cyclic reactions

It is worth mentioning that the Gibbs–Thomson potential is very large in nanoscale materials [24]. Because of the negative curvature of the nanoditch, the Gibbs–Thomson potential can be approximated by

$$\mu_{-r} = \mu_{\infty} \exp \frac{\gamma \Omega}{(-r)kT} \quad (1)$$

where μ_{∞} is the chemical potential of a flat surface, γ is the surface energy of SiC per unit area, and Ω is the molecular volume of SiC, and kT has the usual meaning of thermal energy. Actually the nanoditches have the morphology of a pulley, so there are two curvatures and the other one is positive and its diameter is slightly less than that of the diameter of the nanowires before etching. We have ignored it in the previous equation. Due to the higher Gibbs–Thomson potential, the interaction between a Pd particle and the nanoditched support is higher than that of an unetched SiC support. Therefore, the nanoditches can not only enhance the interaction between the metal component and the support, but also avoid the reaction between them.

The catalyst test results in Fig. 3 show that with the unetched SiC, the temperature for complete conversion of methane is 410°C, which is slightly higher than that of the etched catalyst. The lower activity of the unetched catalyst is also due to the larger size of active Pd particles. More importantly, however, the activity of the unetched catalyst decreases rapidly. The methane conversion at 410°C decreases from the initial 100 to 82% after 10 cyclic reactions (see Fig. 3b). The TEM result shows that the size of Pd particles has an obvious increase. The average size of Pd particles has increased to 17.4 nm, and some of them even increased to 42 nm after 10 cycles (see Fig. 3c). These results indicate that the migration and the coalescence of the Pd particles have occurred seriously on the smooth surface of the unetched support.

From the previous results, we conclude that the nanoditches can improve the activity and stability of the Pd/SiC catalyst. Naturally, we wonder if the size of the nanoditches may influence the catalyst. According to the literature [19, 22], a higher temperature or longer reaction time can enhance the etching and produce deeper ditches. Figure 4a shows the TEM image of the Pd/SiC catalyst that employed the 85°C etched nanowires as the support. From the image, it can be seen that the etching has produced 10-nm-thick fins standing on the nanowires, and the nanoditches between neighboring fins are obviously deeper than the 60°C etched and have a size of about 20 nm. The Pd particles embedded in these nanoditches are found to have diameters ranging from 10 to 15 nm, averagely 12.9 nm, which is even larger than that on the unetched nanowires.

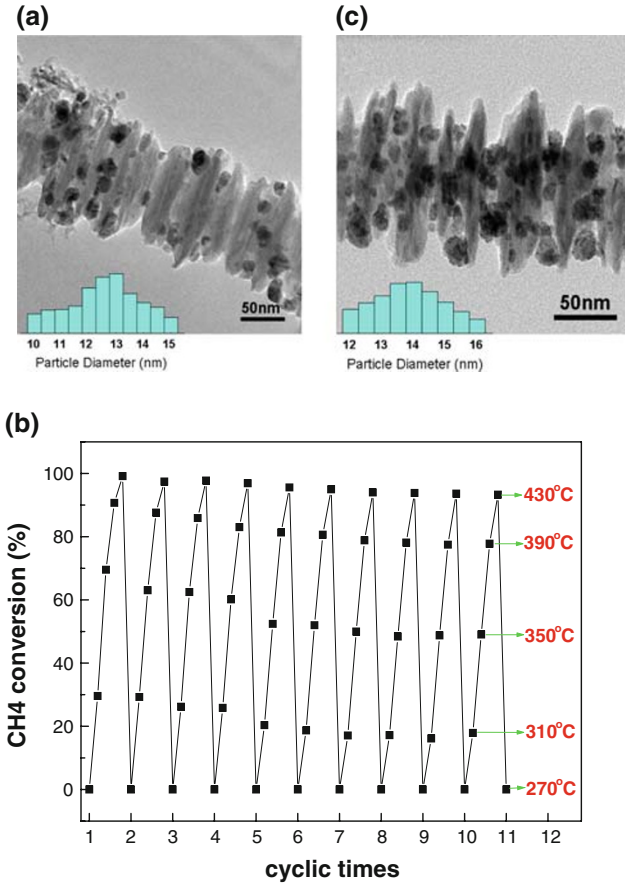


Fig. 4 TEM images of fresh (**a**) and used (**c**) catalyst (etching at 85°C for 30 min) showing that the Pd nanoparticles can easily migrate and grow in the calcination process whereas remain their size during the reaction on the situation of deep etching; (**b**) the test results showing that the activity and stability of catalysts only have a slightly decrease after 10 reaction cycles

As seen in Fig. 4a, the etching has resulted in the formation of an ordered fin-like structure. The space between neighboring fins is so large that it can accommodate more than one initially formed Pd particles. During the catalyst calcination (500°C, 4 h), the fins can hinder the migration and growth of the Pd nanoparticles along the SiC nanowires axis. However, the large place between two fins cannot anchor Pd nanoparticles and prevent their migration perpendicular to the nanowires axis. As a result, those initially formed particles in one nanoditch can migrate together and become larger particles.

The catalyst test results show that the 100% conversion temperature of methane on the 85°C etched catalyst is 430°C and the methane conversion decreases to 93% after 10 reaction cycles (Fig. 4b). It is worthwhile noting that the catalytic activity is lower than the unetched catalyst, but the stability is better. Figure 4c is a TEM image of the catalyst after 10 reaction cycles. From the image, the Pd particles have a size distribution from 12 to 16 nm and an average size of 14.7 nm, indicating that the particle size only has a slightly increase during the reaction cycles. These results demonstrate that the fin-like structures still can limit the growth of the Pd particles during the catalytic reaction and therefore improve the catalyst stability.

From the previous results, it can be found that the catalytic activity of Pd/SiC catalysts depends on the size of Pd nanoparticles. The smaller the particle size, the higher the catalytic activity. The Pd particles supported on the 60°C etched nanowires have an average diameter of 2.9 nm, and the corresponding catalyst can completely convert methane at 390°C ($T_{100\%}$). On the 85°C etched nanowires, the average particle size increases to 12.9 nm. Correspondingly, its $T_{100\%}$ increases to 430°C. The unetched catalyst has an average Pd particle size of 6.7 nm and a $T_{100\%}$ of 410°C; however, the Pd particles easily become large and thus result in the increase of $T_{100\%}$. Therefore, the etched nanostructures provide an effective route to control the size of metal particles and to restrict the growth of nanosized catalyst particles.

According to previous literature, α-SiC and β-SiC have different resistances to acid etching [22]. Krasotkina et al. reported that α-SiC is stable in the boiling mixture of HF, HNO_3, and H_2SO_4 acids, whereas β-SiC could be easily etched by the mixture [25]. Lutsenko et al. also found that β-SiC could be completely dissolved in the mixture of HF and HNO_3, whereas industrial SiC powder consisting of both α-SiC and β-SiC could be etched only partially [26]. Many researchers have demonstrated that SiC materials are potentially excellent catalyst support for various reactions [27], such as dehydrogenation of *n*-butane [28], selective oxidation of H_2S [29], catalytic reforming of hydrocarbons [30], ammonia synthesis [31], partial oxidation of methane [32, 33], and others [34, 35, 36]. However, these applications are greatly limited by the weak interaction between metal nanoparticles and SiC support. In other words, the metal particles migrate and grow easily on the inert SiC surface, and therefore decreasing the catalyst stability. Since industrial powder-like SiC materials usually contain numerous stacking faults in their crystallites, they can be etched selectively to produce a ditched morphology and larger specific surface area, which will make SiC more suitable to be the material for catalyst support. Therefore, the present work demonstrates that the etching method can be employed to design novel nanostructured catalyst with high activity and excellent stability. It enables a wide application of SiC materials as catalyst supports.

Conclusion

In heterogeneous catalysis and fuel cell fields, the size control and stabilization of metal nanoparticles is still a

challenging problem. In this work, we firstly produced different-size nanoditches on the SiC nanowire surface by adjusting etching conditions, and then assembled Pd nanoparticles into the nanoditches to obtain a nanostructured Pd/SiC catalyst. The present results indicate that the metal particle size can be controlled and stabilized by the nanoditches. The nanostructured catalyst exhibits excellent stability in the catalytic combustion of methane, which is a strongly exothermic reaction. The catalyst can keep the methane conversion of almost 100% whereas the unetched one has an obvious decline in the catalytic activity from 100 to 82% after ten cycles. The excellent catalytic stability originates from the limitation of the nanoditches to the migration and growth of Pd nanoparticles.

Acknowledgments The work was financially supported by NSFC (Ref: 20973190), Taiyuan City (Ref: 08121011), Shanxi Province (Ref: 2008011014-1), and an in-house research project of SKLCC from MOST (Ref: SKLCC-2008BWZ010).

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